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Proton Magnetic Resonance Studies of the Solvation Shell of Mg^{2+} in Methanol. Solvation Number and Exchange Rate

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Abstract: The exchange rate of methanol molecules in the solvation shell of magnesium ion in acidic anhydrous methanol was determined between −50 and 35° from the broadening of OH proton magnetic resonance signals of the free and bound methanol. The CH_3 signal of the coordinated methanol, which was hidden behind the bulk CH_3 line, can be observed by the addition of cupric ion to the solution. From the temperature behavior of this signal, it can be concluded that ligand exchange, rather than simple OH-proton exchange, is the dominant process under the conditions of the experiment. The first-order rate constant and activation parameters at 25° are: $k = 4.7 \times 10^3$ sec^{-1}, $\Delta H^{\ddagger} = 16.7$ kcal mole^{-1}, and $\Delta S^{\ddagger} = 14$ eu. From relative intensity measurements of the signals at −80 and −19.2°, the solvation number of the magnesium ion was calculated to be 6. Similar experiments with lithium, calcium, strontium, and barium perchlorates failed to show a separate solvation-shell signal down to −110°. For these ions ligand exchange is apparently rapid down to that temperature.

In this paper we report a proton magnetic resonance study of the solvation of Mg^{2+} ions in anhydrous solutions of magnesium perchlorate in methanol. Our principal aim was to obtain accurate measurements of the solvation number and of the rate of ligand exchange. The work is a follow-up of a note by Swinehart and Taube,[2a] in which they reported that magnesium perchlorate in methanol at −75° exhibits separate resonance peaks for the methanol in the solvation shell of the magnesium ion and for that in the bulk solvent.

The following articles, reporting recent related work, are quoted for purposes of reference and will also provide a key to earlier work. Swinehart, Rogers, and Taube[2b] obtained results for the solvation numbers and the exchange rates for several metal ions, including Mg^{2+} in methanol. They used rather intricate and difficult isotope dilution techniques. Eigen's relaxation methods[3] have yielded a vast amount of data on the rate of substitution of water molecules in the first solvation shell of metal ions by various anions. The observation that these rates are relatively insensitive to the nature of the anion has led to the interpretation that the rate corresponds to the exchange rate of the coordinated water molecules, but this is subject to further substantiation. Swift and Connick[4] have used the broadening of the ^{17}O nmr lines in isotope-enriched aqueous solutions of paramagnetic transition metal ions to measure the rate of ligand exchange. Luz and Meiboom[5] were able to determine the solvation numbers and exchange rates for Co^{2+} and Ni^{2+} in methanol by a more direct nmr technique. For these systems the CH_3 and OH protons of the coordinated methanol were observed as separate signals at lower temperature. The advantage of using methanol, rather than water, as a solvent is that the solutions may be cooled to far lower temperature to slow down the exchange rate into a range accessible to the nmr technique. Obvious disadvantages, on the other hand, are our poor knowledge of the chemistry in this medium in general and the difficulty of handling and the instability of its anhydrous solutions.

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(1) To whom inquiries should be addressed.

(2) (a) J. H. Swinehart and H. Taube, *J. Chem. Phys.*, 37, 1579 (1962); (b) J. H. Swinehart, T. E. Rogers, and H. Taube, *ibid.*, **38**, 398 (1963).

(3) M. Eigen and L. de Maeyer, "Technique of Organic Chemistry," Vol. VIII, Part II, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1961, Chapter 18.

(4) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 37, 307 (1962).

(5) Z. Luz and S. Meiboom, *ibid.*, **40**, 1058, 1066, 2686 (1964).

In the present investigation of the solvation of Mg^{2+} ions in methanol, the OH protons of the bound methanol give a resonance peak which is well separated from the bulk OH peak. The CH_3 peaks of bound and bulk methanol, on the other hand, so nearly coincide that they cannot be observed separately. A technique using selective broadening of the bulk methanol by the addition of paramagnetic Cu^{2+} ions makes it possible to observe the two peaks separately and thus establish that the exchange in acidified solutions is predominantly ligand, rather than proton, exchange. In basic solutions a base-catalyzed exchange takes place, which, because of experimental difficulties, has not at present been studied quantitatively. It has not been established whether this exchange involves whole ligand molecules or only protons.

The nmr spectra of neutral or acidified (up to 0.05 *M*) solutions of anhydrous $LiClO_4$, $Ca(ClO_4)_2$, $Sr(ClO_4)_2$, and $Ba(ClO_4)_2$ in methanol at temperatures as low as −110° failed to show any separate solvation-shell signal or exchange broadening of the bulk methanol signals. Presumably, these ions exchange their solvation shell at a much higher rate than Mg^{2+}.[6] Absence of chemical-shift data prevents us from setting accurate lower limits on these exchange rates, but the rates are very probably faster than 10^4 sec^{-1}. Preliminary experiments with $Al(ClO_4)_3$ showed definite signals for its solvation shell, and this system is the subject of further studies.

Experimental Section

Materials. Hexahydrated magnesium perchlorate prepared from magnesium carbonate and perchloric acid was treated with decolorizing carbon and recrystallized three times from doubly distilled water. It was then dehydrated as follows. First, free water was removed from the wet salt in a vacuum desiccator at room temperature, and the resulting cluster was pulverized. The pulverized dry hexahydrated salt was then heated in a vacuum desiccator, made of a large bore Pyrex tube provided with an external heating tape. A vacuum connection at the bottom maintained a pressure of about 5 mm, with a slight leak of dry nitrogen gas introduced at the top through a needle valve. To avoid melting of the salt, the temperature was kept initially at 50°, then raised to 140° ($Mg(ClO_4)_2 \cdot 6H_2O$ mp 147°), where approximately half of the dehydration took place, and finally kept at 200° until constant weight was attained, in about 12 hr. One equivalent of anhydrous magnesium perchlorate thus prepared contained *ca.* 1×10^{-3} equiv of strong base (presumably MgO or $MgCO_3$) and 1.001 equiv of magnesium as titrated by standard EDTA solution using Eriochrome Blue Black B indicator.[7]

^{25}Mg was obtained from Oak Ridge National Laboratory as magnesium oxide of 91.54% isotopic abundance. The material was dissolved in a slight excess of concentrated perchloric acid and a small amount of water, evaporated by moderate heat, and then dehydrated as described for the regular magnesium perchlorate. The anhydrous $^{25}Mg(ClO_4)_2$ thus obtained had an appreciable gray tint, but was used without further treatment.

Anhydrous perchlorate salts of lithium, calcium, strontium, and barium were prepared from the corresponding hydrated salts obtained from G. F. Smith Chemical Co. by the same procedure of recrystallization and dehydration.

Anhydrous methanol was prepared following the method described by Grunwald, Jumper, and Meiboom.[8]

A stock solution of perchloric acid in methanol was made of 73.6% aqueous perchloric acid and anhydrous methanol.

Anhydrous cupric perchlorate solution in methanol was prepared by refluxing equivalent quantities of anhydrous cupric sulfate and barium perchlorate in methanol under a moisture-free atmosphere, and by separating the resulting insoluble barium sulfate. A copper titer of the resulting solution was determined by iodometric titration.[9]

All the starting materials and the other chemicals employed were of reagent grade quality.

Typical solutions for the nmr measurements were prepared by weighing out the anhydrous magnesium perchlorate in a stoppered vessel and dissolving it in anhydrous methanol and other anhydrous stock solutions[10] as needed, allowing minimum contact with the atmosphere. The sample solutions were sealed in standard nmr tubes and stored in a Dry Ice–methanol mixture when not in use. Samples used for the measurements were always less than a few days old.

Nmr Measurements. All the nmr spectra were recorded at 60 MHz with a Varian HR-60 spectrometer. This spectrometer was modified as described in ref 8. In the present version of the field-control circuitry, either a frequency sweep or a field sweep can be used. The latter was preferred in the accurate relative intensity measurements; it precludes any changes in radio-frequency level or phase with sweep, effects which are present to some degree when using the frequency sweep. Absence of saturation was checked by recording each spectrum at two different precalibrated radio-frequency levels. The ratio-frequency attenuator and recorder gain control were both calibrated under the operating conditions using the maximum height of the viscosity-broadened methyl signal of a sample solution at low temperature. Integration of the signal was performed by measuring the area under the recorded spectra with a planimeter.

The rates of ligand exchange were obtained by fitting the observed line widths and line shapes of the OH peaks in slow-passage spectra with computer-calculated spectra for a range of exchange rates. The calculations were based on the Bloch equations,[12] which were set up for a quadruplet for the solvation-shell resonance and a singlet for the bulk OH resonance (the underlying quadruplet structure of the latter is averaged out by rapid proton exchange between the bulk molecules in the acidified solutions used). The only nonroutine aspect of these calculations is the treatment of the "natural" line widths (*i.e.*, the line widths excluding the exchange contribution). This point arose because at the lower temperatures, at which the exchange rate is so slow that the solvation shell exhibits a well-defined quadruplet structure, it proved impossible to achieve an exact fit of the observed line shape and a calculated one based on a simple 1:3:3:1 Lorentzian quadruplet with an equal natural line width of its components. In the observed quadruplet, the two central lines are narrower than the outer lines. This is obvious in Figure 2 from the relative heights of the peaks. Actually, appreciable differences in the line widths of the individual components are to be expected, as has been shown both theoretically[13] and experimentally.[14] A rigorous theory exists,[13] but for the present purpose an intuitive argument, similar to that given by Anderson,[14] suffices. We note that the 1:3:3:1 OH quadruplet can be considered to be made up of a 1:1:1:1 quadruplet corresponding to a total spin of $^3/_2$ of the CH_3 protons, superposed on a doublet of 2:2 intensity corresponding to a total spin of $^1/_2$ of the CH_3 protons. Such a separation is meaningful, because it is to be expected that transitions between states of different total spin

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[6] It could be argued that for these ions the solvation-shell resonance would not be observed either if the chemical shift between the OH peaks were too small or if fast proton exchange between solvation shell and bulk took place. These possibilities have been ruled out by experiments with added paramagnetic Cu^{2+} ions. This technique revealed neither an OH nor a CH_3 resonance of the solvation shell in the ions under discussion, while it was successful in locating the solvation CH_3 resonance in Mg^{2+}.

[7] A. I. Vogel, "Quantitative Inorganic Analysis," 3rd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 434.

[8] E. Grunwald, C. F. Jumper, and S. Meiboom, *J. Am. Chem. Soc.*, **84**, 4664 (1962).

[9] Reference 7, p 358.

[10] The methanolic solution of perchloric acid described above contained *ca.* 3 equiv of water per equivalent of perchloric acid. However, only very small quantities of this solution were added to the nmr sample, and the effect of this minute quantity of water accompanying perchloric acid was always insignificant. Anhydrous perchloric acid in alcohols is explosive and forms ether or ester,[11] and hence could not be used.

[11] "Gmelins Handbuch der Anorganischen Chemie," Vol. 6 ("Chlor"), 8th ed, Verlag Chemie, Berlin, 1927, p 372.

[12] For an excellent review, see C. S. Johnson, Jr., in "Advances in Magnetic Resonance," J. S. Waugh, Ed., Academic Press Inc., New York, N. Y., 1965.

[13] F. Bloch, *Phys. Rev.*, 102, 104 (1956); A. G. Redfield, *IBM J. Res. Develop.*, 1, 19 (1957).

[14] W. A. Anderson, *Phys. Rev.*, **102**, 151 (1956).

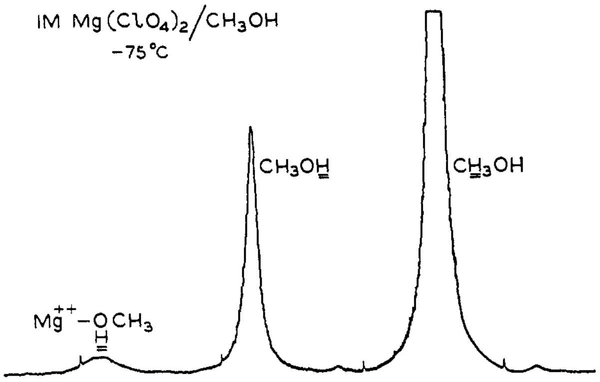

Figure 1. Nmr spectrum of a 1 *M* solution of $Mg(ClO_4)_2$ in anhydrous methanol at −75°. The four small sharp peaks are frequency markers spaced by 100 Hz. The field increases from left to right. The interpretation of the different peaks is indicated by underlining the protons involved. The top of the methyl peak is off-scale. The ^{13}C satellites of the methyl resonance are evident as two weak peaks on either side of the main CH_3 peak.

are relatively rare (these transitions would be strictly forbidden if the time-dependent perturbations seen by the three CH_3 protons were coherent). As the longitudinal relaxation of the CH_3 protons contributes to the line width of the OH peaks through the scalar spin–spin coupling, the 1:1:1:1 lines must be assigned a line width, $1/(T_2)_1$, which differs from that assigned to the 2:2 lines, $1/(T_2)_2$. Moreover, since the two relaxation times are governed by the same correlation time, it is reasonable to assume that their ratio, $r = (T_2)_1/(T_2)_2$, is independent of temperature.

Summarizing the conclusions of the above argument, in the theoretical calculations we represent the solvation-shell resonance by a 1:1:1:1 quadruplet of line width $1/(T_2)_1$ and a superposed 2:2 doublet of line width $1/(T_2)_2$. We assume that the ratio, *r*, of these line widths is independent of temperature. A value of $r = 0.5$ gave an excellent agreement between calculated and experimental line shapes. The importance of the above refinement can be judged from the fact that a change in *r* of ±10% resulted in a noticeable discrepancy between observed and calculated line shapes. That the refinement is essential for accurate rate measurements in the present case, while it (hopefully) can be disregarded in much of the earlier rate work, is of course the result of the large line width (comparable to the spin–spin splitting) of the solvation-shell resonance. This line width, incidentally, is due to the increased size of the complex and the higher viscosity at low temperatures, both factors increasing the correlation time.

Results and Discussion

Figure 1 shows the nmr spectrum of an anhydrous 1 *M* solution of magnesium perchlorate in methanol at −75°. The lines are relatively broad because of increased viscosity at the high salt concentration and low temperature. Figure 2 shows the OH quadruplet of the solvation shell on an expanded frequency scale and under conditions of smaller line width. The well-defined quadruplet structure indicates that, under the conditions of Figure 2, exchange of the OH protons of the solvation methanol is slower than about 1 sec^{-1}. This is true both for exchange with the bulk solvent and for exchange within a solvation complex. In contrast, under the same conditions proton exchange between bulk methanol molecules is very rapid; the bulk OH and CH_3 signals do not exhibit multiplet structure.

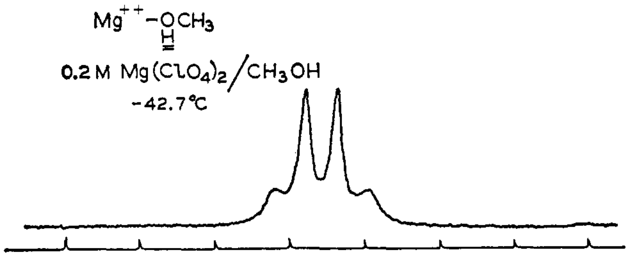

Figure 2. Detail of the OH quadruplet of the methanol in the Mg^{2+} solvation shell. The spectrum is of a 0.2 *M* $Mg(ClO_4)_2$ solution in anhydrous methanol at about −42.7°. At this temperature the line width is a minimum; at lower temperatures viscosity increases, while at higher temperatures ligand exchange sets in. The frequency markers (on a separate trace) are 10 Hz apart.

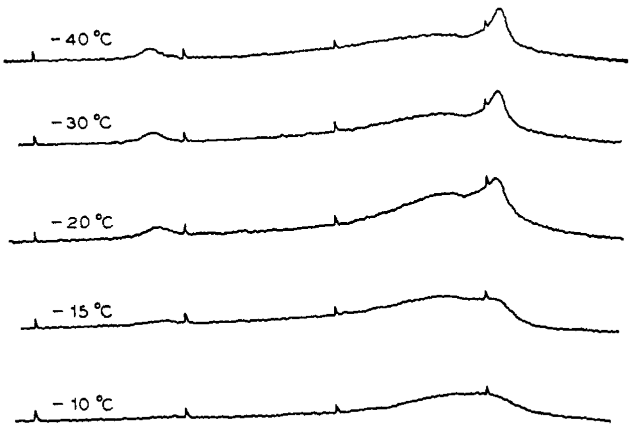

Figure 3. Spectra of a solution containing 0.4 *M* $Mg(ClO_4)_2$ and 0.006 *M* $Cu(ClO_4)_2$ in methanol. The frequency markers are 100 Hz apart. The very broad line extending over the right half of the spectra is due to methanol exchanging rapidly between bulk and Cu^{2+} solvation shell. At the lower temperatures the separate OH and CH_3 peaks of the methanol coordinated with Mg^{2+} are evident.

The separate solvation shell signal is observed only below 0° and in acidified solution.[15] This signal is sharpest around −40°. At higher temperatures it gradually broadens and above about 10° solvation and bulk OH resonances coalesce into a single averaged-out line, which sharpens as the temperature is raised further. This behavior is the one expected from increasingly rapid exchange between solvation and bulk OH. When the solution was not acidified, or when it was made basic by the addition of sodium methoxide, no separate solvation-shell signal was observed down to the freezing point of the solution at *ca.* −110°.

A separate signal for the methyl protons of the coordinated methanol molecules was not observed in the above spectra. The reason is that its position is very little shifted from that of the CH_3 protons of the bulk methanol, and its peak is obliterated by the latter. This was verified by intensity measurements, as well as by experiments with added Cu^{2+}, which will be discussed below. Similar findings were made for $Mg(ClO_4)_2$ in anhydrous ethanol; a separate OH signal, but no separate CH_2 or CH_3 signals, for the coordinated ethanol was observed.

Solutions Containing Cu^{2+}. When anhydrous cupric perchlorate in methanol was added to the system, the spectra shown in Figure 3 were observed. The methanol molecules coordinated with the paramagnetic Cu^{2+} exchange rapidly with the bulk methanol (much faster than those coordinated with Mg^{2+}), but not directly with those in the magnesium solvation shell. Thus the

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(15) Commercially available anhydrous magnesium perchlorate, as well as the material prepared as described in the Experimental Section, contained an appreciable amount of strong base, so that enough perchloric acid to neutralize it had to be added in order to see the solvation-shell signal.

bulk OH and CH_3 signals are strongly broadened, but the Mg^{2+} solvation-shell signals only slightly so. As a result the signals of the coordinated methanol appear as relatively sharp lines on top of the very broad bulk signals. The expected doublet structure in the CH_3 signal is unresolved because of broadening by the Cu^{2+}, but the interpretation is confirmed by the relative intensities. The areas under the two signals give the expected ratio of 3:1. This rather ingenious technique of finding the "hidden" solvation-shell signals using paramagnetic ions is due to Jackson, Lemons, and Taube.[16] This technique offers a valuable way of determining whether the exchange of OH protons of the solvation shell is due to the exchange of the whole ligand molecules, or of the protons only. This question cannot be answered from the OH signals only. In Figure 3 it is seen that OH and CH_3 signals of the solvation shell broaden and disappear at the same time as the temperature is raised. This clearly demonstrates that the whole methanol molecule, rather than just the OH proton, is exchanging with the medium.

Unfortunately, this technique could not be applied to the base-catalyzed exchange, because Cu^{2+} was precipitated before the solution was made basic enough to broaden either signal. Manganous ion can also act similarly and is less acidic than Cu^{2+}, so that the solution can be made basic enough to broaden the OH signal of the solvation shell. However, Mn^{2+} broadens solvation-shell signals extensively and in no case could the solvation-shell CH_3 signal be resolved from the bulk signals. Other common transition metal ions, such as Co^{2+} or Ni^{2+}, do not exchange the solvation shell fast enough to be useful for this purpose, and we have not been able to find a suitable ion in the basic solutions.

Solvation Number. The solvation number of the magnesium ion in anhydrous methanol was determined at −80 and −19.2° from the molar ratio of $Mg(ClO_4)_2$ and methanol in the solution and the ratio of the areas under each signal in the spectrum. At the temperatures chosen, the OH signals were broad enough to allow reasonably accurate area measurements (at −80° the width is due to higher viscosity and at −19.2° to exchange broadening). At the lower temperature, the CH_3 signal was also broad, and an accurate measurement of its area was possible. The CH_3 result agreed well with the areas of the other two signals and thus provided a check on the accuracy of the area measurements. At the higher temperature the CH_3 signal is not broadened by exchange and was too sharp for an accurate area determination.

The results of the area measurements are summarized in Table I. In each case at different concentrations and two different temperatures, the solvation number is calculated to be almost exactly 6. A noninteger solvation number seems to be incompatible with the relatively slow ligand-exchange rate observed, and hence the value of 6 is favored.

Table I. Results of Area Measurements

		Area under peaks[a]					
Temp, °C	Molar ratio,[b] S/M	Solvation OH A_s	Bulk OH A_b	CH_3 A_m	$3(A_s + A_b)$	Solvation no.[c] N	N'
−80	25.53	7.16	24.8	97.0	95.9	5.7	6.0
−80	20.42	4.72	10.85	45.3	46.7	6.2	5.8
−19.2	21.67	3.16	8.32	...	...	6.0	...

[a] The areas are given in arbitrary units and should be compared within each row only. [b] S is the number of moles of methanol and M the number of moles of magnesium perchlorate in the solution. [c] N is calculated from the OH peaks: $N = (S/M)A_s/(A_s + A_b)$, while N' is calculated from the CH_3 peak (which accounts for both bulk and solvation methanol) and the bulk OH peak: $N = (S/M)(A_m - 3A_b)/A_m$.

As to the geometry of the hexacoordination, the clean symmetry of the quadruplet signal points to a regular, *i.e.*, octahedral arrangement. It may be argued that a highly distorted octahedral species will also exhibit a simple quadruplet if the ligands interchange positions rapidly within the solvation shell, so as to average out the different chemical shifts. Although this possibility cannot be ruled out completely, such a model would imply that the methanol molecules farthest from the Mg^{2+} center would be relatively weakly bound and would be expected to exchange faster than the low rate actually observed. It appears to be reasonable to conclude that Mg^{2+} has six methanol molecules in a regular octahedral configuration in its first solvation shell under the conditions studied.

Another inference to be drawn from these observations is that even at rather high concentrations ($[Mg^{2+}] \cong 1\ M$ and $[ClO_4^-] \cong 2\ M$) and low temperature (−80°) in this relatively nonpolar solvent, no appreciable "close" ion association takes place. Penetration of perchlorate ion into the first solvation shell of Mg^{2+} would certainly have decreased the solvation number observed.

Solutions Containing Water. When a small amount of water is present in the system, it appears to be preferentially coordinated to magnesium ion.[2a,17] At a temperature of about −40° the spectrum shows the rather complex fine structure shown in Figure 4. The complex band at the left appears to be a superposed pair of quadruplets, A and B. Spectra of samples containing less water than that of Figure 4 ($[H_2O]/[Mg^{2+}] < 1$) show that signals B and C increase at the same rate as water content is increased, with the ratio B/C approximately constant at 2.5. The signals B and C are thus assigned to methanol OH and water protons, respectively, in $Mg(CH_3OH)_5OH_2^{2+}$, while signal A is assigned to the hydroxyl groups of $Mg(CH_3OH)_6^{2+}$. When the mole ratio $[H_2O]/[Mg^{2+}]$ is increased, other lines, presumably for other mixed complexes, are observed to appear in the spectrum (D). It is interesting to note that, in Figure 4, the multiplet B is somewhat more broadened than A at −44°. This indicates a faster exchange of ligands in the monohydrated ions than in the fully methanolated ones. However, no quantitative measurements of ligand-exchange rates were attempted for the mixed complexes, and the remainder of this paper will be devoted to the anhydrous system only.

Chemical Shift. Precise knowledge of the chemical shift, δ, between the solvation-shell OH signal and the bulk OH signal as a function of temperature is required for an accurate determination of the temperature dependence of the exchange rate. All the points in Figure

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(16) J. A. Jackson, J. F. Lemons, and H. Taube, *J. Chem. Phys.*, 32, 553 (1960).

(17) The water also acts as a buffering agent and reduces the pH of the solution sufficiently to give a separate solvation-shell signal even when some sodium methoxide was added to the solution.

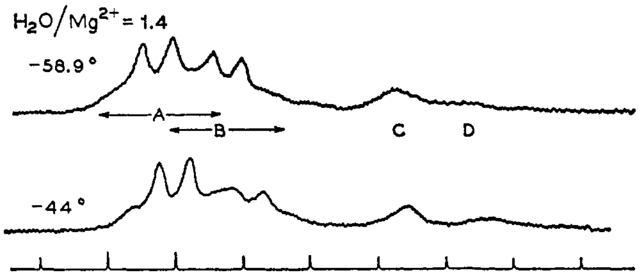

Figure 4. The low-field part of the spectrum of a solution of 0.25 *M* $Mg(ClO_4)_2$ and 0.35 *M* H_2O in methanol. The frequency markers are 10 Hz apart. The spectrum consists of two overlapping quadruplets, A and B, of which A is interpreted as the hydroxyl resonance of $Mg(CH_3OH)_6{}^{2+}$ and B the hydroxyl resonance of $Mg(CH_3OH)_5(OH_2)^{2+}$. The line C is due to the water resonance of the latter complex, and D presumably to complexes with two or more water molecules.

5, except the one for the highest temperature, were obtained by direct measurement of the slow-passage spectra. The high-temperature point represents the value obtained from the coalescence temperature of the two signals and will be discussed in the next section. These data are all for the magnesium concentration used for the rate measurements (*ca.* 0.24 *M*); no attempt was made to determine the concentration dependence of the chemical shift.

The sudden dip shown by a broken line in Figure 5 is due to the onset of exchange and has the magnitude and direction predicted from the solution of the Bloch equations for two exchanging lines.[12] Under such conditions the separation between the two lines does not represent the actual chemical shift, and interpolated values (the solid line in Figure 5) were used for the rate determinations.

It is well known that the OH signal of pure methanol shifts markedly toward higher field as the temperature is raised, while the CH_3 signal remains relatively constant. This is attributed to the hydrogen bonding of the OH protons. For the methanol containing magnesium perchlorate, the bulk OH signal shows the expected shift with temperature, while the OH signal of the coordinated methanol shifts in the same direction but to a smaller degree. Accordingly, there is a small but significant change in the relative chemical shift of the two OH signals. It is not immediately clear whether this has any direct relation to the extent of the hydrogen bonding of the coordinated methanol molecules with the surrounding molecules of a presumed second solvation shell. From a consideration of the acidity of hydrogen atoms, such a hydrogen bond is expected to be stronger than that between bulk methanol molecules, since the acid dissociation constant of $Mg(CH_3OH)_6{}^{2+}$ is 10^3 times greater than that of methanol.[18]

The spin–spin coupling constant J_1 of the coordinated methanol was determined from the OH quadruplet in the temperature range where it was well resolved (−52.7 to −37.6°). A value of 4.46 Hz was found independent of temperature. This value was used in the computation of the apparent transverse relaxation times over the entire temperature range, as will be described below.

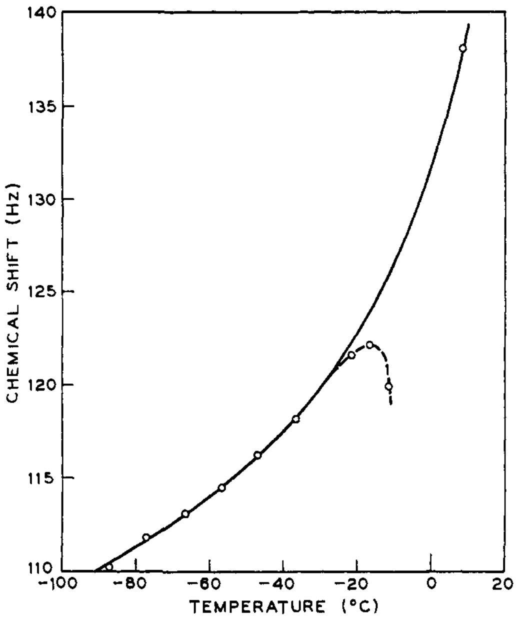

Figure 5. Relative chemical shift (δ) of the bulk OH signal and the solvation shell OH signal as a function of temperature. The graph is for anhydrous methanol containing 0.24 *M* $Mg(ClO_4)_2$.

Solutions from ^{25}Mg-Enriched Material. Magnesium in natural isotopic abundance contains 10% of the spin $^5/_2$ nucleus ^{25}Mg, the remainder being spin zero ^{24}Mg and ^{26}Mg. The question can be raised whether a spin–spin interaction between the ^{25}Mg ion and the OH protons of the coordinated methanol exists. An appreciable interaction would have to be allowed for in the calculation of the solvation number from peak intensities as well as in the rate calculations from the line widths. In order to answer this question, solutions enriched to 91.54% in ^{25}Mg were obtained as described in the Experimental Section. Nmr spectra for these solutions made at −40° showed a solvation-shell quadruplet identical as to line width, spacing, and intensity with the quadruplet obtained in a solution made from natural abundance Mg. It is concluded that the spin–spin coupling between the ^{25}Mg ion and the OH protons in its solvation shell is very small and does not contribute appreciably to the measured line widths.[19]

Measurements of Exchange Rate. A very low concentration of acid appears to be sufficient to suppress the base-catalyzed exchange. In two solutions whose pH's[18] at room temperature were about 7 and 11, respectively, the base-catalyzed exchange below −40° was too slow in the former, and too fast in the latter, to be measured by nmr. All the measurements reported below were made in acidified solutions, in which the base-

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(18) By potentiometric measurements the pK_a of Mg^{2+} in 0.1 *M* $Mg(ClO_4)_2$ in anhydrous methanol was found to be 14.0, whereas the pK_m, the self-ionization constant of methanol, is 16.92 at 25°.[8] A regular assembly of glass electrode, saturated aqueous KCl reference electrode, and the pH meter was calibrated against anhydrous methanol buffered by substituted and unsubstituted benzoates and gave a sufficiently stable and reproducible linear pH reading for the range employed (pH ~7–11). The pK_a value was calculated from the pH of the mixtures of $Mg(ClO_4)_2$ and $NaOCH_3$ in anhydrous methanol taking into account the strong base which co-exists with anhydrous $Mg(ClO_4)_2$.[15]

(19) Another explanation of the absence of splitting is that a nonzero spin–spin interaction is averaged to zero by rapid quadrupole relaxation of the ^{25}Mg nucleus. As the electric quadrupole moment interacts with the gradient of an electric field, rapid relaxation would mean that the geometry of the solvated ion is such as to lack a center of symmetry. We consider this possibility as highly improbable, but even if it were true our results for the solvation number and exchange rates would not be affected, although the idea of a regular octahedral arrangement of the coordination methanol would of course not be right.

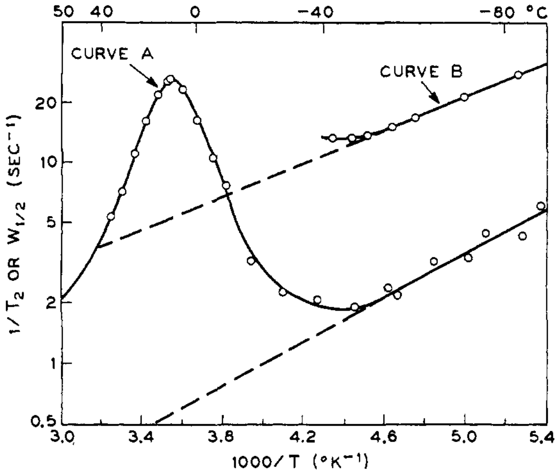

Figure 6. Line widths of the bulk OH line (curve A) and of the solvation-shell OH peaks (curve B) as a function of temperature. In curve B the quantity plotted is $1/(T_2)_1$, defined in the text. The concentration of $Mg(ClO_4)_2$ is 0.236 *M* for curve A and 0.238 *M* for curve B.

catalyzed reaction is of no importance. We did not succeed in making a thorough study of the base-catalyzed reaction for the following reasons. There is the difficulty, already mentioned, of distinguishing proton exchange from ligand exchange in the basic solutions, and the necessary measurements in nearly neutral solutions require the use of buffering agents, which might form complexes with Mg^{2+} and complicate the interpretation. Attempts to buffer the solutions by Mg^{2+} itself failed because of its low acidity.

Two *ca.* 0.2 *M* $Mg(ClO_4)_2$ solutions with 0.001 and 0.002 *M* $HClO_4$ added, respectively, gave identical spectra over the temperature range studied, demonstrating that the exchange in this range of acid concentration is independent of pH. Further addition of $HClO_4$ apparently did not affect the exchange rate, but, to avoid complications due to the trace of water accompanying the acid,[10] all the rate measurements were made in solutions containing *ca.* 0.001 *M* $HClO_4$. The rate measurements were made over as wide a temperature range as possible (about −55 to +35°). This of course improves the accuracy of the activation parameters obtained and also provides a check that a single mechanism of ligand exchange is dominant under the conditions of the experiment.

Solvation-Shell Signal. Figures 1 and 2 illustrate the solvation-shell peaks observed at the lower temperatures. As discussed in the Experimental Section, the quadruplets were interpreted as the sum of a Lorentzian 1:1:1:1 quadruplet with line width $1/(T_2)_1$, superposed on a 2:2 doublet with line width $1/(T_2)_2$. A simple computer program for summing Lorentzian lines was written and used to plot calculated multiplet shapes on the above assumptions. Agreement between measured and calculated line shapes was obtained for $r \equiv (T_2)_1/(T_2)_2 = 0.5$, independent of temperature, and $1/(T_2)_1$ values given by curve B in Figure 6. The linear part of this curve, extrapolated to higher temperatures as indicated by the broken line, together with the value $r = 0.5$, was used to obtain the "natural" line widths of the solvation-shell peaks required in the rate calculations described below. The rise of curve B at the higher temperatures indicates the onset of ligand exchange. Because the exchange is slow, the excess line width (*i.e.*, the distance of the measured points from the natural line width given by the broken line) can be equated to the rate of exchange, $1/\tau_B$ (where τ_B is the average lifetime of a specific methanol molecule in the solvation shell).

Bulk OH Signal. In addition to the solvation-shell signal, the "bulk OH" peak (which at low temperatures is the free-solvent signal, and at higher temperatures the coalesced signal from free solvent and solvation shell) also provides values for the exchange rate. In Figure 6, curve A gives the width at half-maximum amplitude, $W_{1/2}$, as a function of reciprocal temperature.[20] At low temperatures exchange broadening can be neglected, and the line width is that of the free solvent. Extrapolation to higher temperatures (the lower broken line in Figure 6) gives the natural line width of the solvent resonance for use in the rate calculations.

As the temperature is increased, exchange broadening sets in and reaches a maximum when the exchange rate is comparable to the chemical shift between solvation shell and free-solvent OH peaks (at about 10°). At still higher temperatures the averaged-out OH peak narrows with increasing exchange rate. For the quantitative interpretation, a computer program to simulate the exchange broadened spectrum was used.[21] This program calculates and plots line shapes based on the Bloch equations, generalized to include exchange terms.[12] Plots were obtained for a series of exchange rates, $1/\tau$, and the widths and shapes of the peaks were compared with those in the experimental spectra to evaluate the $1/\tau$ giving the best fit. The natural line widths required in the computations were obtained from the broken lines in Figure 6, and the chemical shift was found from the plot in Figure 5.

As mentioned before, the high-temperature point in Figure 5 was obtained from the maximum of curve A in Figure 6. The procedure was as follows. For a trial chemical shift, the line width of the bulk peak was computed for a number of rates, $1/\tau$, and its maximum value determined graphically. The value of the maximum width was then plotted as function of the assumed chemical shift, and that chemical shift adopted for which the calculated and observed maximum width agreed.

Effect of Mg^{2+} Concentration. In Figure 7 are given the results of measurements to establish that the rate of ligand exchange is first order in magnesium concentration. The measurements were made at −4.5°. This is a convenient temperature because it is still in the range where the lifetime broadening of the bulk OH peak is a good approximation, so that the rate of exchange can be obtained directly from the excess width

$$\frac{1}{\tau_A} = \frac{P_B}{P_A}\frac{1}{\tau_B} = \frac{1}{T_2'} - \frac{1}{T_2} \tag{1}$$

where τ_A is the residence time of methanol in the bulk between exchanges, τ_B is the residence time in the solvation shell, $1/T_2'$ is the observed line width of the bulk OH peak, $1/T_2$ is its natural line width (obtained from the

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(20) We use here the half-width, $W_{1/2}$ (in units of radians per second), rather than $1/T_2$, because at intermediate exchange rates the lines are not Lorentzian, and T_2 is not strictly defined. At both low and fast rates $W_{1/2}$ is identical with $1/T_2$.

(21) This program was written by M. Cocivera, to whom we are indebted for its use. It is written in FORTRAN for the IBM 7094 computer and provides plots from an on-line Stromberg-Carlson 4020.

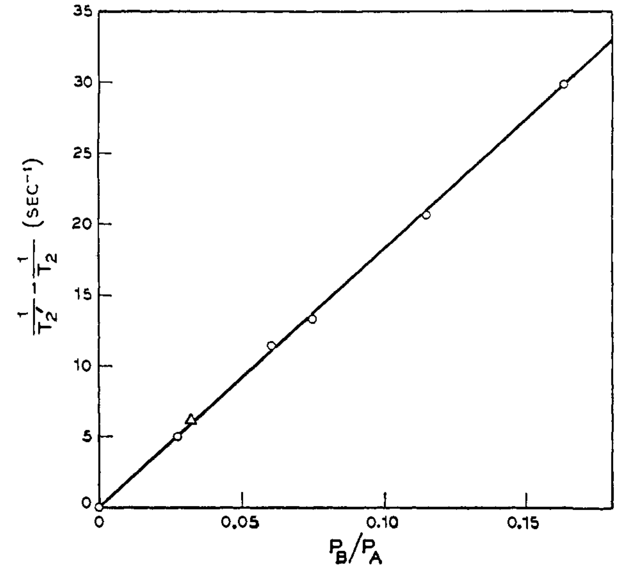

Figure 7. Exchange broadening of the bulk methanol line as a function of the mole ratio of free methanol to Mg^{2+} solvation-shell methanol, at a temperature of −4.5°. The triangle refers to a solution to which $Ca(ClO_4)_2$ was added in approximately the same concentration as the $Mg(ClO_4)_2$ present.

lower broken line in Figure 6), and P_A and P_B are the methanol mole fractions in the bulk and in the solvation shell, respectively. Figure 7 indicates that $1/\tau_A$ is proportional to P_B/P_A, and from eq 1 it follows that $1/\tau_B$ is constant. Thus it can be concluded that the exchange rate is first order in magnesium concentration and ionic-strength independent. As a further check on the latter conclusion, a solution containing equal amounts of $Mg(ClO_4)_2$ and $Ca(ClO_4)_2$ was also measured. The result is indicated by the triangle in Figure 7.

The question is relevant whether small amounts of water, which could not be completely excluded and which solvates the magnesium preferentially to form monohydrate complexes, could have affected the measured rates. A comparison of solutions containing different amounts of water (up to a few thousandths molar) showed no detectable effect on the measured rate.

Temperature Profile. The results for the exchange rate constant, $k = 1/\tau_B$, are summarized in Table II. Figure 8 gives a plot of log ($1/\tau_B$) *vs.* $1/T$ over a wide range of temperature (−53 to 35°) and rates (an approximately 10^5-fold change). This remarkably linear Arrhenius plot assures us that there is only one dominant exchange mechanism, ligand exchange, over the entire temperature range studied. Thus the rate constant, k, is assigned to the following first-order process

$$Mg(CH_3OH)_5(C^*H_3OH)^{2+} + \text{bulk } CH_3OH \xrightarrow{k} Mg(CH_3OH)_6{}^{2+} + C^*H_3OH$$

although the mode of participation of the incoming methanol molecule in the transition state (SN1 or SN2) is not clear from these results. The rate constant and the activation parameters calculated for 25° are $k = 4.7 \times 10^3$ sec^{-1}, $\Delta H^{\ddagger} = 16.7$ kcal mole^{-1}, and $\Delta S^{\ddagger} = 14$ eu.

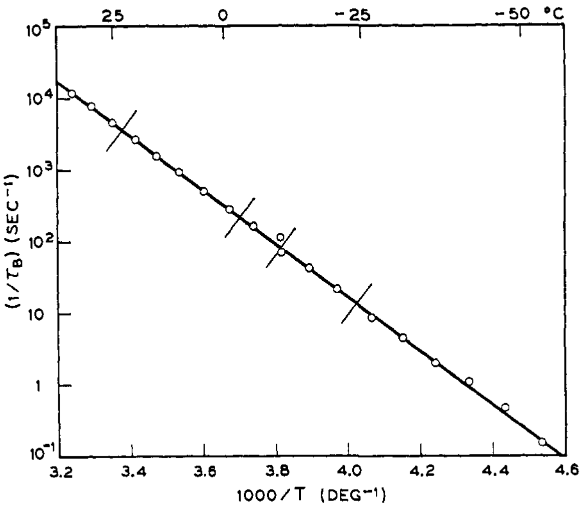

Figure 8. Arrhenius plot of the rate of methanol exchange between Mg^{2+} solvation shell and free methanol. The quantity τ_B is the average lifetime between exchanges of one specific methanol molecule in the solvation shell.

As mentioned earlier, ultrasonic studies of the kinetics of ion association in water by Eigen,[3] and more recently by Atkinson and Kor,[22] have led to multistep mechanisms in which the rate-determining last step is the formation of a close ion pair, the rate of this process being determined solely by the rate of elimination of a solvent molecule from the first solvation shell. This picture is in accordance with the observation that the association rate is independent of the nature of the incoming anions. It is also supported by the fact that the rate found by the ultrasonic method is close to the rate of hydration water exchange found by Swift and Connick[4] from ^{17}O nmr measurements in aqueous solutions of paramagnetic metal ions. These facts seem to support an SN1 mechanism for the ligand substitution. In the present case we cannot make a similar comparison, because no data on ultrasonic absorption in methanol solutions are available.

Table II. Rate Constants

Temp, °C	$k = 1/\tau_B$, sec^{-1}	P_B	Method of rate calculation
−52.7	1.5×10^{-1}	0.0580	Broadening of solvation shell OH quadruplet peaks (slow exchange approximation)
−47.6	4.6×10^{-1}		
−42.7	1.1		
−37.6	2.0		
−32.5	4.3		
−27.3	8.4		
−21.5	2.2×10	0.0578	Solvation-shell OH collapsed quadruplet (slow exchange approximation)
−16.5	4.2×10		
−11.4	6.9×10		
−11.4	1.1×10^2	0.0572	Bulk OH signal (slow exchange approximation)
−6.0	1.6×10^2		
−1.1	2.8×10^2		Bulk OH and coalesced signal (complete solution of Bloch equations)
4.1	5.0×10^2		
9.1	9.3×10^2		
14.3	1.6×10^3		
19.5	2.7×10^3		
24.7	4.6×10^3		Coalesced OH signal (fast exchange approximation)
29.9	7.9×10^3		
35.2	1.2×10^4		

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(22) G. Atkinson and S. K. Kor, *J. Phys. Chem.*, **69**, 128 (1965).

Swinehart, Rogers, and Taube[2b] measured rate constants by isotope dilution experiments for methanol solutions containing 0.9 mole of H_2O per 1 mole of $Mg(ClO_4)_2$. Their results are 1.12×10^{-3} sec^{-1} at $-96.9°$ and 1.87×10^{-2} sec^{-1} at $-82.5°$. From these two values they calculated the activation parameters, $\Delta H^{\ddagger} = 12.5 \pm 2.0$ kcal $mole^{-1}$ and $\Delta S^{\ddagger} = 4 \pm 4$ eu. When our results are extrapolated to $-82.5°$, $k = 3.5 \times 10^{-4}$ sec^{-1} is obtained. This is about $^1/_{50}$th of the quoted results of Swinehart, Rogers, and Taube. This discrepancy is presumably due to the acceleration of the exchange by water, as already noted by these authors, and their rates and activation parameters are probably predominantly for the monohydrated complex. The predominance of the monohydrate when water is present is seen in Figure 3. This figure also indicates that at $-44°$ the monohydrate still exchanges relatively slowly, and that at this temperature the ratio of the exchange rates for the hexamethanolate and the monohydrate is larger than the ratio 1/50 quoted above for $-82.5°$. An order of magnitude calculation shows that a consistent picture is obtained if the activation energy of 12.5 found by Swinehart, Rogers, and Taube is roughly that for the monohydrate, while the higher figure of 16.7 of the present work is that for the hexamethanolate.

The clean linearity of the Arrhenius plot extending to the higher temperature also sheds some light on the solvation number at these temperatures. If there were any drastic change in the structure of the solvation shell, say a change in solvation number, one would expect it to show up in the behavior of the rate constant with the temperature. Absence of any such obvious effect in the Arrhenius plot indirectly argues against such a drastic change. Also, in view of the relatively low rate of exchange observed, it appears to be well justified to conclude that the first solvation shell for Mg^{2+} exists as a well-defined entity and contains six methanol molecules in the temperature range studied.

The pronounced effect of pH on the nmr signals, which we have not been able to study closely because of the difficulties stated earlier, prohibits the extrapolation of the observed rates to neutral or basic media. Fast proton exchange in basic solution is not at all unexpected, but the possibility of a base-catalyzed ligand exchange is also not ruled out and requires further investigation.

Acknowledgments. We thank Dr. M. Cocivera for making his computer program available and for many discussions. The high performance of the nmr spectrometer used in this work is largely due to the contributions of Mr. R. C. Hewitt.

Reactions of Isomeric Ions[1]

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Contribution from Esso Research and Engineering Company, Baytown Research and Development Division, Baytown, Texas. *Received November 12, 1966*

Abstract: It is shown in this paper that the butyl ions produced by ionic reactions in *n*-butane react differently from the butyl ions produced by ionic reactions in isobutane with propylene, 2,2,4-trimethylpentane, and 1-pentene. The ions which are formed in the two gases do not have the same structure and do not rearrange in times short compared with a microsecond.

In a previous study on the kinetics of ionic reactions in hydrocarbons, it was reported for *n*-butane and isobutane that the major reactions were hydride-transfer reactions which produced $C_4H_9^+$ as the dominant ions for both compounds.[2] It was not possible then to determine whether the two butyl ions were the same or different, but, intuitively, one would think that they were initially different, even if *sec*-$C_4H_9^+$ rearranged to *t*-$C_4H_9^+$ during the time of the experiments (10^{-6} sec). It is difficult to determine directly the structures of ions produced by electron impact, although indirectly it has been possible to establish that isomeric ions may have different heats of formation[3a] and it has also been possible to observe differences in ionization potential for isomeric radicals.[3b] It is the purpose of this paper to show that it is possible to observe by high-pressure mass spectrometry different reactivities for isomeric ions and hence differentiate between structures.

Ausloos and co-workers[4] have performed radiation studies on hydrocarbon systems in which they have interpreted some of their results in terms of several ion-molecule reactions. From experiments with deuterium-labeled compounds, information was derived concerning the reactivities of different positions for attack by several ions and the structures of these ions. The ionic intermediates, however, are not directly observable in these experiments, although analysis of the final products gives unambiguous determination of the labeled positions. For example, the formation of CD_3CDHCD_3 in mixtures of $(CH_3)_3CH$ with $(CD_3)_3CD$

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[1] Presented in part at the Southwest Regional American Chemical Society Meeting, Albuquerque, N. M.

[2] M. S. B. Munson, J. L. Franklin, and F. H. Field, *J. Phys. Chem.*, **68**, 3098 (1964).

[3] (a) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957; (b) F. P. Lossing and J. B. deSousa, *J. Am. Chem. Soc.*, **81**, 281 (1959).

[4] (a) R. P. Borkowski and P. J. Ausloos, *J. Chem. Phys.*, **38**, 36 (1963); (b) R. P. Borkowski and P. J. Ausloos, *ibid.*, **39**, 818 (1963); (c) P. Ausloos and S. G. Lias, *Discussions Faraday Soc.*, **39**, 36 (1965); (d) S. G. Lias and P. Ausloos, *J. Chem. Phys.*, **43**, 2748 (1965); (e) P. Ausloos, S. G. Lias, and A. A. Scala, Advances in Chemistry Series, No. 58, American Chemical Society, Washington, D. C., 1966, pp 264–277.